

THE FLUORINATION OF NON-POLAR CHLORIDES
AND
THE THERMOCHEMISTRY OF HALOGEN
EXCHANGE REACTIONS

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The author
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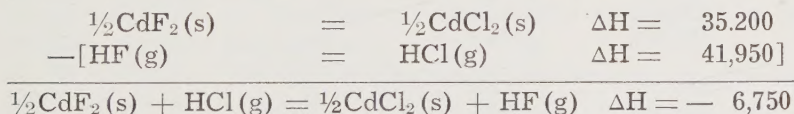
INTRODUCTION

The difficulties of obtaining and using elemental fluorine have made the halogen exchange reaction the most practical means for the preparation of many anhydrous fluorides. Many chlorine-fluorine exchange reactions have been reported in the literature but a theoretical or systematic approach has not been attempted.

DISCUSSION

The quantity of free energy data applicable to this problem is too limited to be of great value.¹ However, approximations may be made by taking advantage of the second law equation, $\Delta F = \Delta H - T\Delta S$, and the fact that ΔS is very nearly constant for many reactions of this type.

Table 1 gives the differences in the heat contents of chloride-fluoride 'couplets', i.e., the heat content of chloride (per equivalent) less the heat content of the fluoride (per equivalent). The algebraic difference of any two couplets gives a complete halogen exchange reaction and its heat of reaction



Approximate standard free energy changes at 25°C. are obtained by applying entropy corrections to the enthalpy changes of the individual couplets. Approximate entropy changes for the couplets have been deduced from a consideration of a few known values and comparisons with other halides. The Latimer entropy equation² which gives accurate values for metal chlorides, bromides and iodides gives values for fluorides that are too high. The values of S given in Table 2 will generally introduce errors in the free energy change not in excess of 600 calories.

TABLE 1

Heat Contents of Chlorides and Fluorides and Their Differences
(At Approximately 25°)

Data (1), (3)

- ΔH° calories/mole		Couplet	$\Delta H^\circ \text{MCl} - \Delta H^\circ \text{MF}$ calories/equivalent
Chloride	Fluoride		
30,300	48,700	$\text{AgF (s)} = \text{AgCl (s)}$	18,400
106,320	131,680	$\text{CsF (s)} = \text{CsCl (s)}$	25,400
105,080	133,240	$\text{RbF (s)} = \text{RbCl (s)}$	28,200
104,361	134,510	$\text{KF (s)} = \text{KCl (s)}$	30,150
33,800	163,000	$\frac{1}{4} \text{CF}_4 \text{ (g)} = \frac{1}{4} \text{CCl}_4 \text{ (l)}$	32,300
25,900	163,000	$\frac{1}{4} \text{CF}_4 \text{ (g)} = \frac{1}{4} \text{CCl}_4 \text{ (g)}$	34,300
92,149	162,490	$\frac{1}{2} \text{CdF}_2 \text{ (s)} = \frac{1}{2} \text{CdCl}_2 \text{ (s)}$	35,200
84,874	156,000	$\frac{1}{2} \text{PbF}_2 \text{ (s)} = \frac{1}{2} \text{PbCl}_2 \text{ (s)}$	35,600
74,950	111,600	$\text{NH}_4\text{F (s)} = \text{NH}_4\text{Cl (s)}$	36,650
98,590	172,700	$\frac{1}{2} \text{ZnF}_2 \text{ (s)} = \frac{1}{2} \text{ZnCl}_2 \text{ (s)}$	37,100
98,330	135,950	$\text{NaF (s)} = \text{NaCl (s)}$	37,600
53,400	131,800	$\frac{1}{2} \text{CuF}_2 \text{ (s)} = \frac{1}{2} \text{CuCl}_2 \text{ (s)}$	39,200
75,000	157,500	$\frac{1}{2} \text{NiF}_2 \text{ (s)} = \frac{1}{2} \text{NiCl}_2 \text{ (s)}$	41,250
205,280	287,900	$\frac{1}{2} \text{BaF}_2 \text{ (s)} = \frac{1}{2} \text{BaCl}_2 \text{ (s)}$	41,300
91,400	216,600	$\frac{1}{3} \text{SbF}_3 \text{ (s)} = \frac{1}{3} \text{SbCl}_3 \text{ (s)}$	41,700
76,900	160,700	$\frac{1}{6} \text{CoF}_2 \text{ (s)} = \frac{1}{2} \text{CoCl}_2 \text{ (s)}$	41,900
22,060	64,000	$\text{HF (g, ideal)} = \text{HCl (g)}$	41,950
88,400	216,600	$\frac{1}{3} \text{SbF}_3 \text{ (s)} = \text{SbCl}_3 \text{ (l)}$	42,700
197,870	289,000	$\frac{1}{2} \text{SrF}_2 \text{ (s)} = \frac{1}{2} \text{SrCl}_2 \text{ (s)}$	45,550
		$\frac{1}{3.3} \text{ (HF)}_{3.3} \text{ (g)} = \text{HCl (g)}$	47,300
97,650	145,570	$\text{LiF (s)} = \text{LiCl (s)}$	47,900
190,600	290,200	$\frac{1}{2} \text{CaF}_2 \text{ (s)} = \frac{1}{2} \text{CaCl}_2$	49,800
150,100	360,100	$\frac{1}{4} \text{SiF}_4 \text{ (g)} = \frac{1}{4} \text{SiCl}_4 \text{ (l)}$	52,500
94,600	256,900	$\frac{1}{3} \text{BF}_3 \text{ (g)} = \frac{1}{3} \text{BCl}_3 \text{ (l)}$	54,100
166,800	329,000	$\frac{1}{3} \text{AlF}_3 \text{ (s)} = \frac{1}{3} \text{AlCl}_3 \text{ (s)}$	54,100
142,500	360,100	$\frac{1}{4} \text{SiF}_4 \text{ (g)} = \frac{1}{4} \text{SiCl}_4 \text{ (g)}$	54,100
153,300	263,800	$\frac{1}{2} \text{MgF}_2 \text{ (s)} = \frac{1}{2} \text{MgF}_2 \text{ (s)}$	55,250
88,300	256,900	$\frac{1}{3} \text{BF}_3 \text{ (g)} = \frac{1}{3} \text{BCl}_3 \text{ (g)}$	56,200
133,000	329,000	$\frac{1}{3} \text{AlF}_3 \text{ (s)} = \frac{1}{3} \text{AlCl}_3 \text{ (g)}$	65,300

TABLE 2

Approximate Entropy Differences for Chloride-Fluoride
Couplets

Couplet	Entropy Difference Calories/equivalent/degree
hydrogen	1.0
metals (except Al, Ca, Mg)	3.5
calcium	6.4
magnesium	7.0
aluminum	8.0

Table 1 (with entropy corrections applied) may be considered as a list of fluorinating agents in decreasing order of strength. Pending further experimental work, it is intended only as a guide to experimental work since overall errors of ± 2000 calories are possible.

EXPERIMENTAL

Anhydrous hydrogen fluoride reacts readily at 25°C. with phosphoryl chloride, phosphoryl dichlorofluoride, phosphorus trichloride, thionyl chloride, silicon tetrachloride, and chlorosulfonic acid yielding hydrogen chloride and the corresponding fluoride. Silicon tetrachloride and chlorosulfonic acid are fluorinated much more rapidly than any of the others. Phosphoryl dichlorofluoride is fluorinated several times as rapidly as its parent compound, phosphoryl trichloride.

In general, the partially fluorinated derivatives are fluorinated much more rapidly than the parent compounds. As a result very little of the intermediate is produced unless by some method it is rapidly removed from the reaction sphere. Booth and coworkers⁴ did this by continuous distillation while reaction was in progress. They used antimony trifluoride as the fluorinating agent.

Phosphoryl dichlorofluoride is prepared in good yield by passing gaseous hydrogen fluoride, diluted with nitrogen, into boiling phosphoryl trichloride and separating the vapors in a fractionating column. Some monochlorodifluoride is also produced. Partial fluorination products of phosphorus trichloride

and thionyl chloride cannot be prepared in this way because reaction is too slow.

Hydrogen fluoride is a very active fluorinating agent. At room temperature it reacts at a moderate or rapid rate with all chlorides with which reaction is thermodynamically possible. The fluorides of the non-polar halides, on the other hand, are unreactive at temperatures up to 100°C. Metal fluorides, also, show chemical reactivities which are not related to their thermodynamic abilities as fluorinating agents. Thus, sodium fluoride fluorinates phosphoryl trichloride rapidly at room temperature whereas potassium fluoride, a much more powerful agent, is almost without effect even at the boiling point.

SUMMARY

1. On the basis of available thermochemical data a scale of reactivity for halogen exchange reactions has been developed and implicitly shown to be useful as a guide to experimental work. It is suggested that this method of handling thermochemical data is applicable to several types of inorganic reactions and that its use makes evident unexpected relations in the properties of elements and compounds. Extended sufficiently, such treatment would contribute substantially to theoretical inorganic chemistry.

2. Anhydrous hydrogen fluoride, at 25°C., is capable of fluorinating several of the non-polar chlorides, namely, phosphoryl chloride, phosphorus trichloride, phosphorus pentachloride, thionyl chloride, chlorosulfonic acid and silicon tetrachloride.

3. Anhydrous hydrogen fluoride reacts with sulfuryl chloride to a very slight extent, if at all. It is not decided whether this is due to equilibrium or to chemical inertness of sulfuryl chloride.

4. The relative rates of reaction of the several non-polar chlorides with anhydrous hydrogen fluoride have been observed roughly.

5. Intermediate products of the fluorination of phosphoryl trichloride by hydrogen fluoride (POCl_2F and POClF_2) can be isolated in good yield by proper control of the conditions of the reaction.

6. Hydrogen fluoride exhibits high chemical reactivity as a fluorinating agent. It reacts with all chlorides with which the exchange reaction has been shown to be thermodynamically possible.

7. Limited evidence indicates the non-polar fluorides to be comparatively unreactive in exchange reactions up to a temperature of about 100°C .

8. Fluorosulfonic acid reacts slowly with phosphoryl chloride, phosphorus trichloride and thionyl chloride at about 100°C . with formation of fluorine compounds but the reactions are not straightforward exchange reactions. Phosphorus trichloride, PCl_3 , for example, give rise to phosphoryl trifluoride POF_3 .

9. A study of halogen exchange reactions involving hydrogen fluoride and the non-polar chlorides in the gas phase was not successful.

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VITA

The author was born at Buffalo, New York, on November 6, 1917. He received his elementary education in public schools of New York, Virginia and Pennsylvania and was graduated from Fosdick-Masten Park High School, Buffalo, in 1935. The author did his undergraduate work at the University of Buffalo from which he was graduated with the degree of Bachelor of Arts in June, 1939. For the following two years he was employed at the Research Laboratories of the Linde Products Company, Tonawanda, New York, which employment he left in September, 1941, to begin graduate work at the University of Illinois.

During his stay at Illinois the author served as a special research assistant for the National Defense Research Committee, 1942-1945; held a University fellowship, first semester, 1945-1946; and a teaching assistantship, second semester, 1945-1946. He received the Master of Arts degree in 1943. He is a member of the Society of Sigma Xi, Phi Lambda Upsilon, Phi Kappa Phi and the American Chemical Society.

